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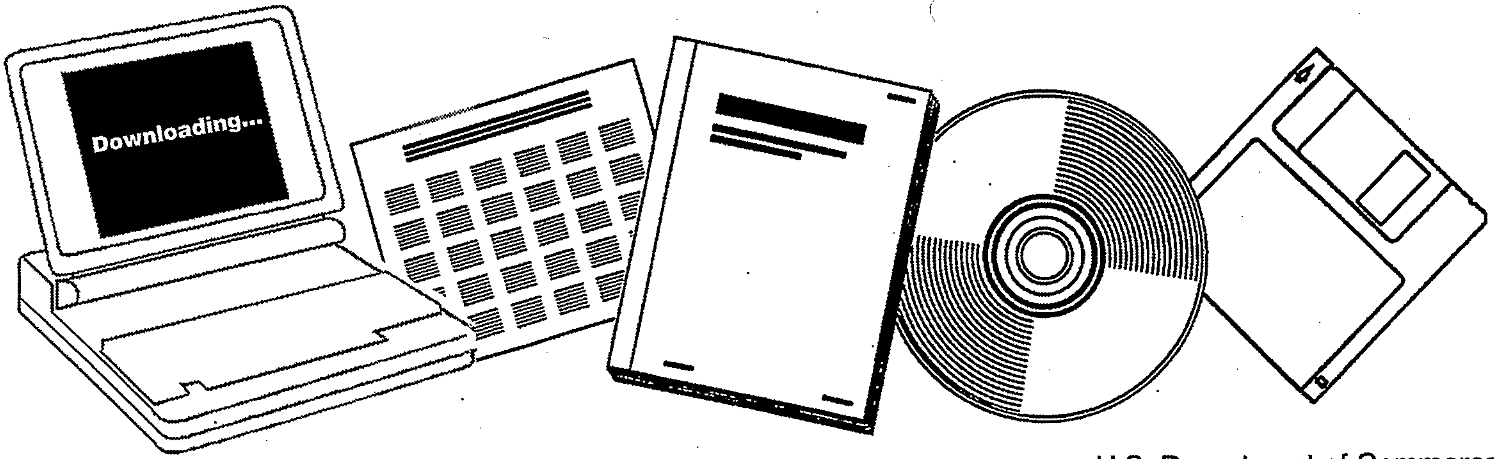

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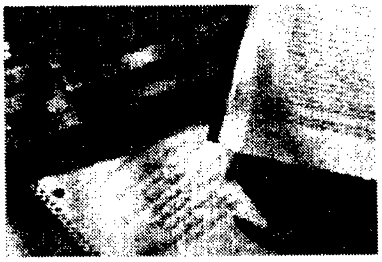

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PROGRESS REPORT

A NOVEL PROCESS FOR METHANOL SYNTHESIS

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 ABSTRACT

A bench-scale reactor is being used to conduct studies of the conversion of synthesis gas to methanol by a novel process. During the last quarter, we investigated the effect of various catalysts on the rate of MeOH synthesis. The success of salts such as alkali formates and carbonates as catalysts indicates the regeneration of the homogeneous catalyst in the presence of Cu-chromite. This could also explain the increased tolerance of the process to the presence of small amounts of H_2O. Mathematical equations were written to explain the non-linearity of the rate (in gmoles/min) with catalyst concentration and the effect of feed flow rate. An on-line gas sampling valve was installed. Efforts are continuing to install an on-line liquid sampling valve. A major difficulty is due to the fact that liquid flow is not continuous.

2.0 INTRODUCTION

An experimental investigation of a new process, developed in our laboratory, for converting synthesis gas to methanol is being carried out. It has significant advantages over the conventional gas phase synthesis in that the recycle of unreacted material can be virtually eliminated and it operates at lower temperatures. The reaction is not significantly poisoned by CO_2 or H_2O. It has been demonstrated that the reaction proceeds with good rates at 150°C and 6.3 MPa pressure. It is likely that the overall reaction proceeds through methyl formate as an intermediate. However, the nature of the mixed catalyst comprised of an alkali methoxide (e.g. KOMe) and Cu-chromite and of the possible intermediates is not well understood. The thrust of this research program is to obtain a better understanding of the reaction and particularly of the role of the catalyst. This information should make it possible to scale up the process.

Two papers have been published[1,2] reporting our studies. One is on the individual reactions: (a) carbonylation of methanol and (b) hydrogenolysis of methyl formate. The other paper is on the concurrent reaction in which a carbonylation catalyst (e.g. potassium methoxide) and a hydrogenolysis catalyst (e.g. Cu-chromite) are used in the same reactor. The current work is part of a three and a half-year project which started in September, 1989.

A paper was presented at the AIChE Summer National

Meeting, San Diego, August 19-22 entitled Synthesis of Methanol in a Methanol-Rich Liquid Phase(3).

In this report, a soluble catalyst refers to an alkali salt (e.g. potassium methoxide) added as a powder to the reactor (the powder is soluble in the solution). The Cu-chromite powder is referred to as a heterogeneous catalyst. A homogeneous reaction is thus one which takes place in the liquid solution (not on the surface of Cu-chromite) and a heterogeneous reaction is one which takes place on the surface of Cu-chromite.

3.0 RESEARCH OBJECTIVES

Principal research objectives are,

1) To determine the effect of alternate catalysts on the synthesis. This will include modified copper chromite catalysts in addition to soluble catalysts in the form of methoxides or similar salts.

2) To determine the nature of the active catalyst in this reaction and the effect of deactivating agents such as CO_2, H_2O and CO.

3) To determine the rate limiting steps in this reaction so that proper scale-up is possible. The effect of catalyst loading and reactor volume are of special importance.

4) To develop mathematical models which can be used to predict the rates of reaction and are suitable for scale-up of the reaction.

4.0 CURRENT WORK

In this quarter, we studied the effect of different soluble catalysts on the rate of MeOH formation. Reaction rate using mixed catalyst systems consisting of equimolar quantities of four different alkali salts with Ba stabilized Cu-chromite are given in Table 1[4].

Table 1: Rate of MeOH Synthesis with Various Soluble Catalysts

Soluble Catalyst	Rate of MeOH Synthesis (gmoles/h/gm cat)	Relative Rcn Rate at 40 hours
Potassium methoxide	0.01905	100
Sodium methoxide	0.01321	68
Potassium carbonate	0.00953	50
Potassium chloride	0.00449	24
None	0.0043	22

All experiments were carried out with 3 gms Cu-chromite at 150°C and 63 atm pressure.

The KOMe/Cu-chromite combination is the best catalyst so far and this is expected from studies on the carbonylation reaction. Sodium methoxide also results in a considerable rate.

The progress of the reaction for these two catalysts is given in Figure 1. The difference in the rates conforms to the idea that the alkali methoxide interacts with the Cu-chromite for hydrogenation activity. The difference may be attributed to the fact that since the ionization potential of K(4.32 V) is less than that of Na(5.12 V), K has a greater ability to generate the methoxide anion. The presence of CO_2 and H_2O should result in the formation of alkali carbonate and formate respectively. These salts may be regenerated to the methoxide in the presence of Cu-chromite which is a good ester hydrogenolysis catalyst by a reaction scheme as shown in Figure 2. A similar scheme has been reported by Bybell et al.(5) for MeOH synthesis on Cu/ZnO catalysts. The Na salts are less soluble than the K salts in the reaction medium and have a tendency to precipitate as a powder leading to a decrease in the MeOH synthesis rate. A white powder of Na formate (determined by pH measurements) was obtained as a precipitate in the run with Na methoxide (NaOMe).

The change in the MeOH synthesis rate with change in the feed H_2/CO flow rate was a surprising result, as reported earlier(6). A similar result was obtained with change in the catalyst loading. Since the hydrogenolysis is the rate-determining step, the rate of MeOH formation should be directly proportional to the amount of catalyst at low loadings. The rates obtained at two different loadings of the mixed KOMe/Cu-chromite catalysts, keeping their ratio the same are presented in Table 2. The progress of the reactions is compared in Figure 3. This might be explained by mass transfer limitations in the liquid, but Liu(1,6) verified that, at the high rate of stirring used, no mass transfer limitations exist in the reactor. A similar effect was obtained by Liu(6) for Cu/Cr/Mn catalysts.

Table 2: Effect of Heterogeneous Catalyst Loading on Rate

K methoxide gmoles/lit	Cu-chromite gm.	Max Rate at 40 hrs gmoles/h/gm cat	MeOH Prod Rate gmoles/min
0.0953	3	0.01905	0.00095
0.1904	6	0.01091	0.001091

The effect of flow rate and catalyst loading on MeOH synthesis rate are related in that the flow rate of gas leaving the reactor decreases when the catalyst loading is increased (more reaction) or feed rate is decreased. The rate of reaction can vary with exit flow rate if a small amount of a deactivating agent is being produced in the reactor, since it can build up to high concentrations when the exit flow rate is low. For both these effects the H_2O composition increased at lower feed flow rate and higher catalyst loading. Since H_2O is a possible deactivating factor, it may be the cause of the lower than expected rates. These observations form the basis of the following equations. Work is underway to determine if this explanation has validity.

EFFECT OF FEED FLOW RATE AND CATALYST AMOUNT ON THE RATE OF METHANOL SYNTHESIS

It has been observed experimentally that the rate of MeOH synthesis per gram of the Cu-chromite catalyst, varies with the flow rate and the amount of the Cu-chromite catalyst present. The following is a possible explanation for the observed effects. It is based on the following assumptions,

1) The rate of MeOH formation decreases as some inhibiting species increases. The presence of CO_2 and H_2O has been found to inhibit the reaction. If it is assumed that at constant temperature and pressure, the rate of reaction varies with the amount of Cu-chromite and the composition in the gas phase of the byproduct, we have,

$$R_1 = K_1 (1 - \alpha y_2) C \qquad (1)$$

where,

R_1 is the rate of MeOH formation, gmoles/min.

K_1 is the reaction constant,

α is a constant,

y_2 is the mole fraction of the deleterious by-product in the gas phase,

C is the concentration of the heterogenous catalyst.

2) The rate of formation of the by-product is proportional to the amount of Cu-chromite catalyst,

$$R_2 = K_2 C \qquad (2)$$

where,

R_2 is the rate of formation of by-product, gmoles.min.

K_2 is the reaction constant.

The rate of formation of MeOH and by-product can also be expressed by material balances. Assuming that the feed to the reactor is a mixture of H_2 and CO in the ratio of 2:1,

$$R_1 = (F_1 - F_2)/3 \tag{3}$$

$$R_2 = F_2\,Y_2 \tag{4}$$

where, F_1, F_2 are the flow rates of gas into and leaving the reactor, mol/min.

The variation of the reaction rate (R_1) with the feed flow rate (F_1) and the amount of heterogenous catalyst (C) is determined by finding (dR_1 / dF_1) with C constant and (dR_1 / dC) with F_1 constant respectively.

Differentiating we get,

<u>Variation of reaction rate with feed flow rate</u>

$$\frac{dR_1}{dF_1} = \frac{1}{\dfrac{F_2}{K_1 \alpha C y_2} + 3} \tag{5}$$

<u>Variation of reaction rate with amount of catalyst</u>

$$\frac{dR_1}{dC} = \frac{K_1(1-\alpha y_2)}{1+\frac{3\alpha C y_2 K_1}{F_2}} \qquad (6)$$

Examination of equations (5) and (6) show the same trend as the experimental data. In equation (5), the right hand side is positive. This implies that the reaction rate increases as F_1 increases and vice-versa. The reaction rate should of course be independent of flow rate unless some change is occuring in the system with flow rate.

Similarly, the reaction rate is expected to increase linearly with the amount of catalyst at the rate $K_1\ (1 - \alpha y_2)$, if y_2 remains constant. The rate as determined from equation (6), however is less, since the denominator on the right hand side is greater than one.

5.0 FUTURE WORK

Studies will be carried out to investigate the activity and nature of the reactions with other catalysts for MeOH synthesis. Different salts will be investigated for their catalytic activity and to test the Cu-chromite regeneration hypothesis. An effort will be made to understand the nature of the reaction, whether heterogeneous or homogeneous followed by a heterogeneous reaction. A new liquid on-line sampling valve is being installed.

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6) Z. Liu, **PhD. Thesis**, submitted to the Department of Chemical and Petroleum Engineering, University of Pittsburgh, 1988.

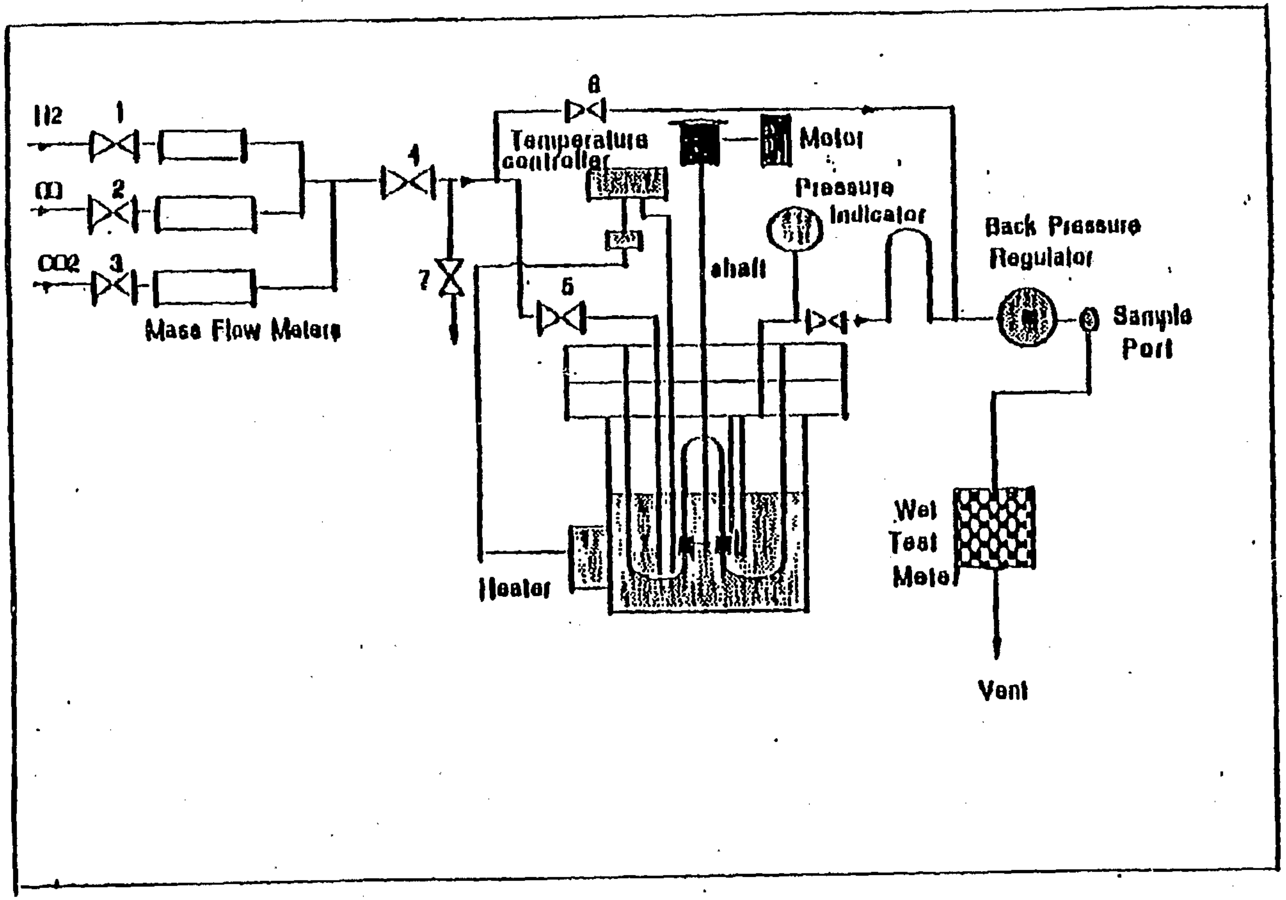

Figure 1. Schematic diagram of experimental equipment.

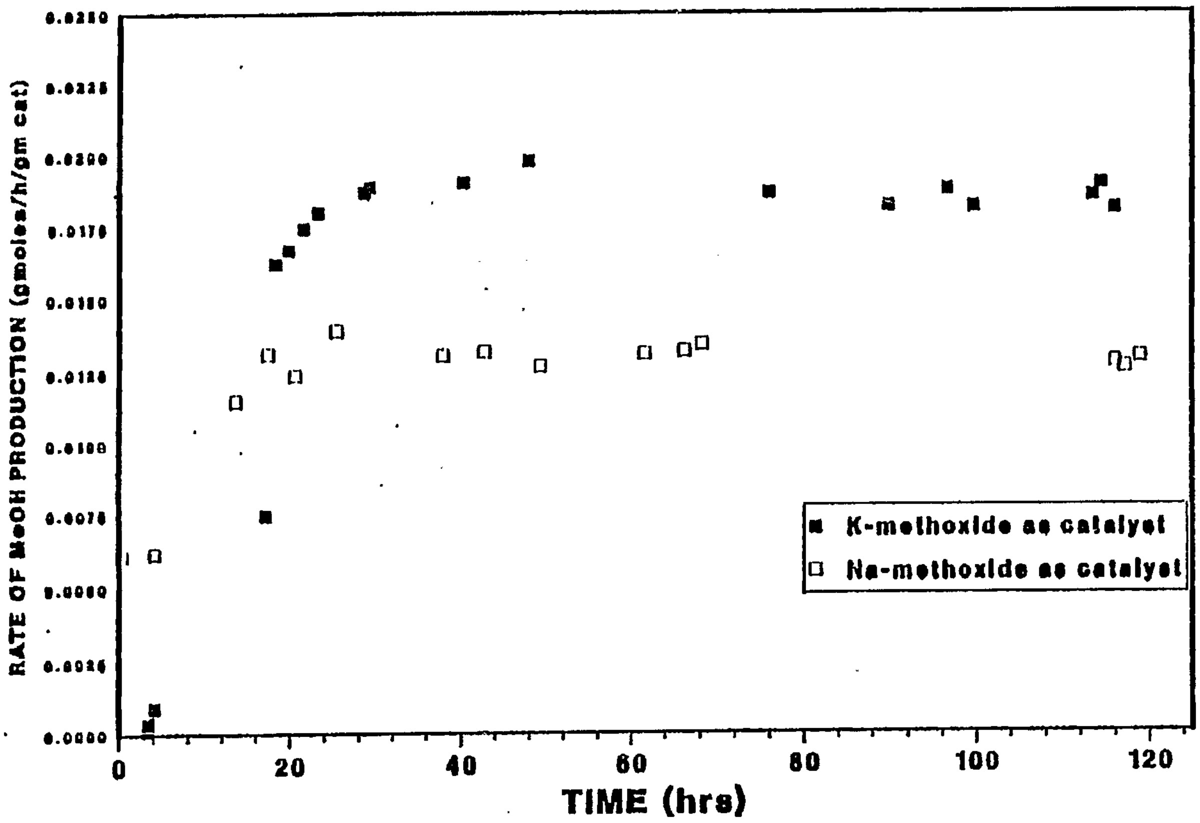

Figure 1: Rate of MeOH Synthesis for K and Na Methoxide Catalysts

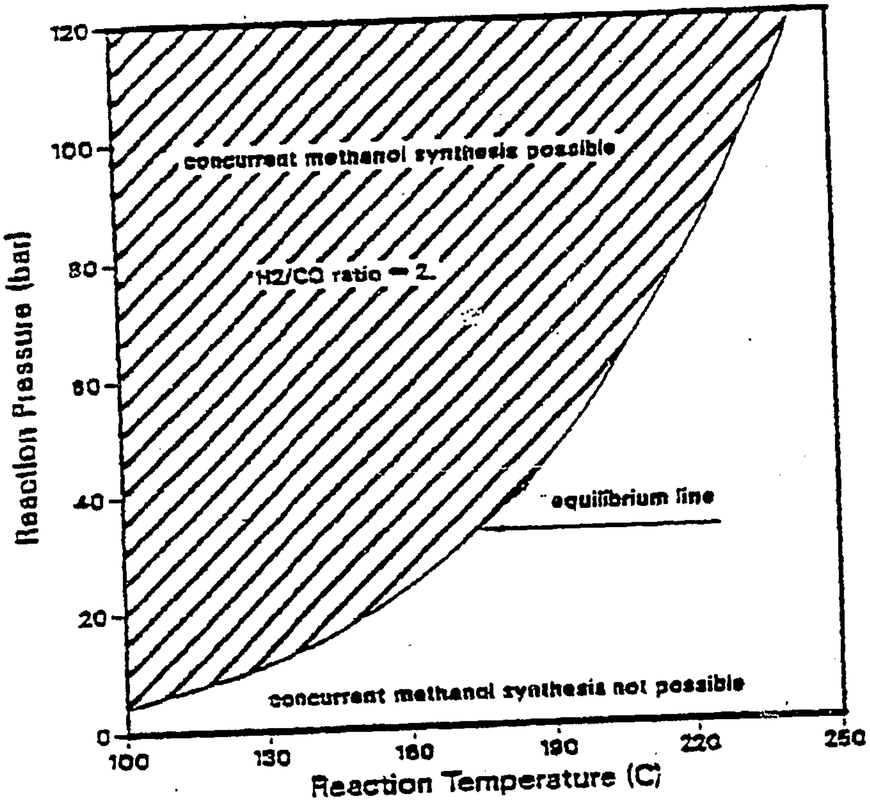

Figure 2. Feasible temperature-pressure regions for concurrent methanol synthesis.

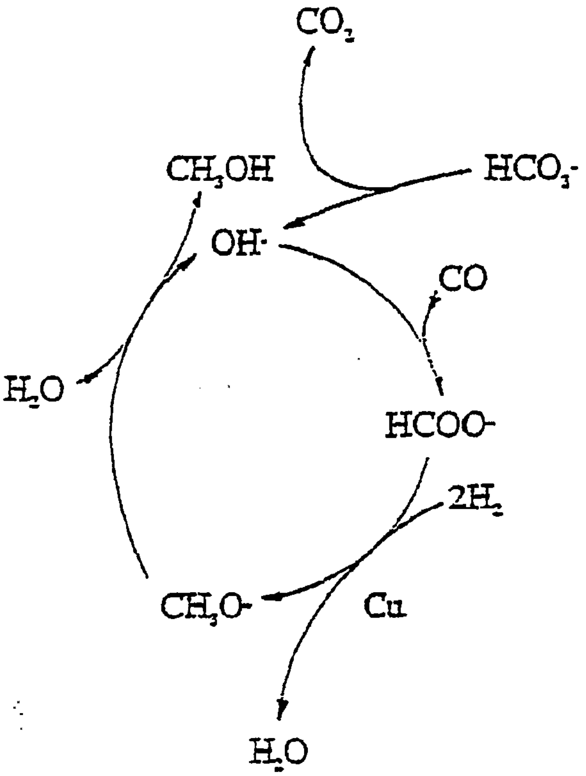

Figure 2: The Copper Chromite Cycle

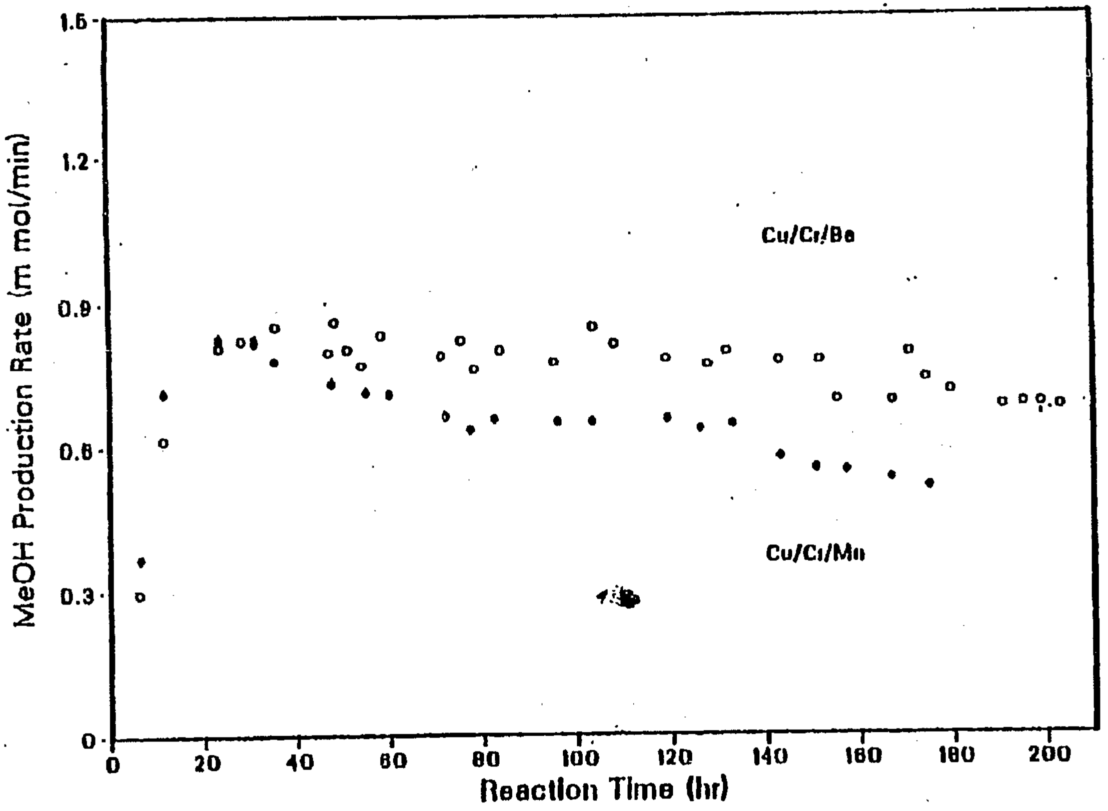

Figure 3. Variation of methanol production rate with time for two copper chromite catalysts. Homogeneous catalyst is potassium methoxide. Reaction conditions: 160°C, 63.5 atm, H_2/CO ratio 1.9, 2 g copper chromite, 0.5 g KOMe, feed rate 100 cc/min

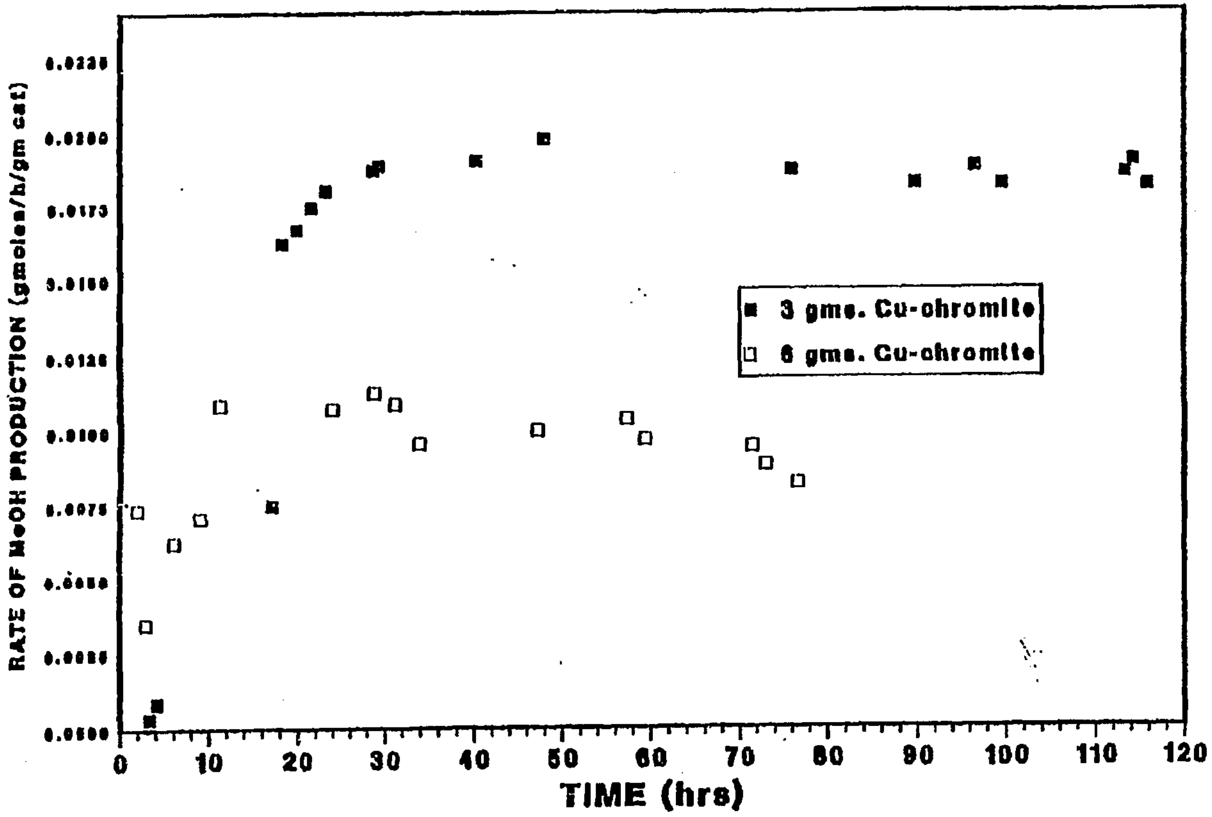

Figure 3: MeOH Synthesis Rate at Different Heterogenous Catalyst Loading

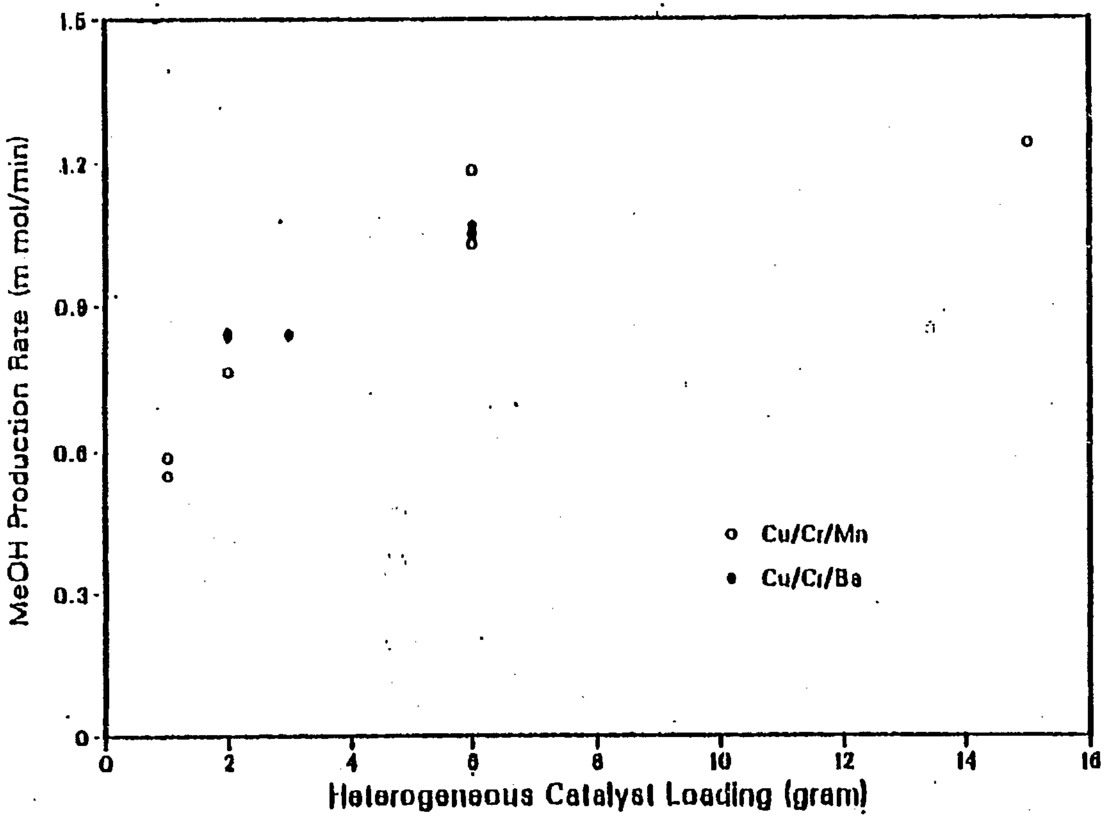

Figure 4. Variation of methanol production at 40 hours with heterogeneous catalyst loading. Reaction conditions: 160°C, 63.5 atm, feed rate 100 cc/min.

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